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(71)Applicant : **HITACHI ZOSEN CORP**
NAKAYAMA YOSHIKAZU

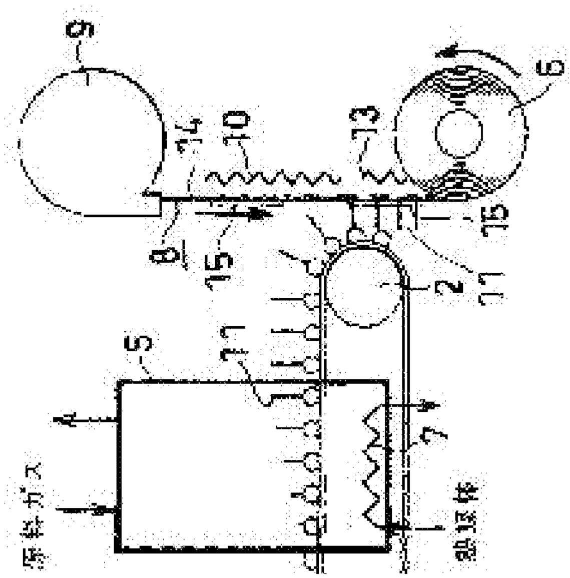
(72)Inventor : **INASUMI CHIKASHI**
SHIOZAKI HIDEKI
FUJITA DAISUKE
NAKAYAMA YOSHIKAZU

(54) ELECTRODE MATERIAL FOR ELECTRON EMISSION ELEMENT USING CARBON NANOTUBE AND ITS MANUFACTURING METHOD

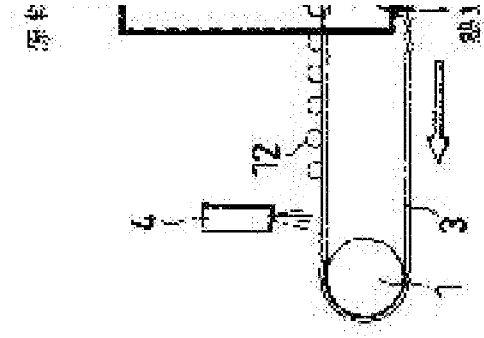
(57)Abstract:

PROBLEM TO BE SOLVED: To provide an electrode material for an electron emission element using carbon nanotubes and its manufacturing method suitable for mass production, profitable in cost, and capable of reducing driving voltage and fining a display screen in use as an electrode for a field emission type flat panel display.

SOLUTION: This electrode material for the electron emission element using carbon nanotubes is formed by transferring the carbon nanotubes 11 each grown from a catalyst particle 12 serving as a core on a substrate 3 to a conductive film 8. The conductive film 8, in which a conductive layer part is patterned, is constructed of an insulating resin sheet 14 and a



predetermined-shape conductor 15 arranged on a sheet 14.



JAPANESE [JP,2004-055158,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS DESCRIPTION OF DRAWINGS DRAWINGS

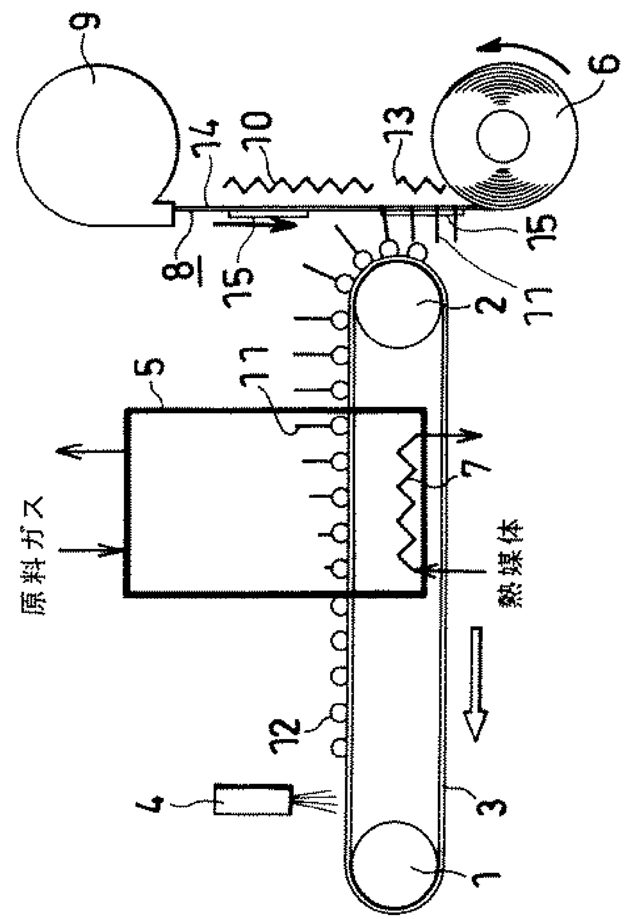
[Translation done.]

* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1]
An electrode material for electron emission elements using a carbon nanotube currently formed by transferring a carbon nanotube grown-up as a core in a catalyst particle on a substrate on a conductive film in which a conductive layer portion was patternized.
[Claim 2]
The electrode material for electron emission elements according to claim 1, wherein a conductive layer is formed of a pencil of a carbon nanotube.
[Claim 3]
A manufacturing method of an electrode material for electron emission elements using a carbon nanotube transferring a carbon nanotube into which a catalyst particle on a substrate was grown up as a core on a conductive film in which a conductive layer portion was patternized.

Drawing selection Representative draw



[Translation done.]

[Claim 4]
A manufacturing method of the electrode material for electron emission elements according to claim 3 forming a conductive layer by a pencil of a carbon nanotube.

[Translation done.]

JAPANESE [JP,2004-055158,A]

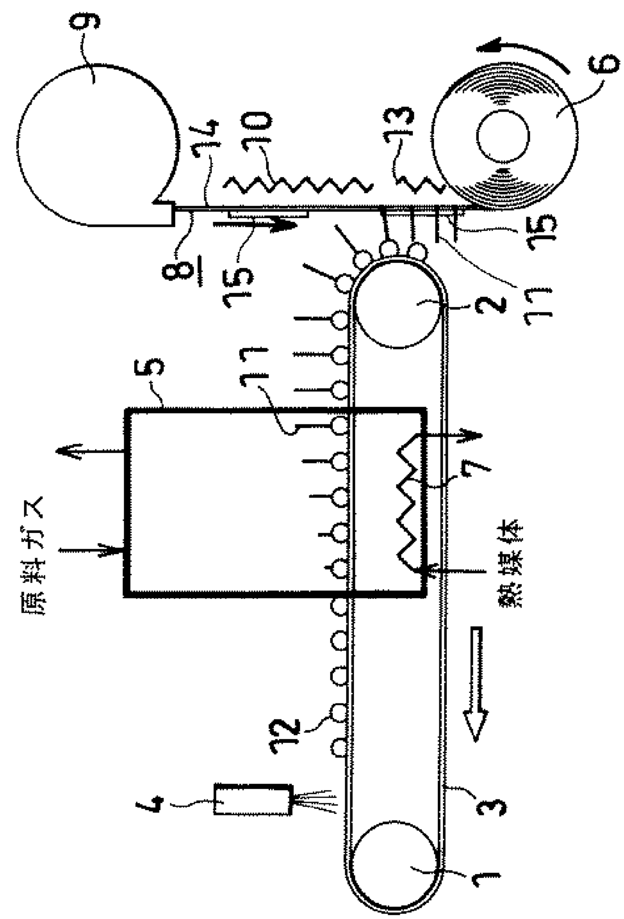
CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]
This invention relates to an electrode material for electron emission elements which used the carbon nanotube, and a manufacturing method for the same. The electrode material for electron emission elements by this invention is preferred as an electrode of a field emission type flat-panel display.
[0002]
[Description of the Prior Art]
Since field emission (field electron emission) is obtained by pulling out high-density tunnel current from the tip of a needlelike emitter, the energy width of an electron beam is also narrow high-intensity. The field emission type flat-panel display (FED) which can realize low power consumption, high-intensity, and a quantity angle of visibility is being developed using this character.

Drawing selection Representative draw



[Translation done.]

[0003]
In the characteristics, such as current density, driver voltage, stoutness, and a life, the carbon nanotube is excellent in the comprehensive target compared with the conventional electron emission raw materials made from silicon or molybdenum, such as the Spindt type emitter and diamond membrane.
It is regarded as the most promising [now] as an electron source for FED.
This is because a carbon nanotube has a big aspect ratio (ratio of length to a diameter), and a sharp tip, and is stably and mechanically tough chemically and excelling in the stability in an elevated temperature etc. is moreover provided with the advantageous physicochemical quality as an emitter material of field emission.
[0004]
The structure of the FED panel which makes a carbon nanotube an electron source is typically shown in drawing 5.
In drawing 5, (41) and (42) are the glass plates of an up-and-down couple.
The electrode (43) used as the negative pole is stuck on the upper surface of a lower glass plate (42), and the carbon nanotube (44) of a large number which become this negative pole (43) with an emitter is formed.
A fluorescence layer (RGB) (45) is provided in the undersurface of an upper glass plate (41), and the aluminum film (46) used as the anode which receives the electron emitted to this undersurface from the tip of a carbon nanotube is stuck on it. Between two electrodes (43) and (46), the grid (47) is provided in these and parallel.
Between a grid (47) and a top glass board (41), Two or more tube support plates (48) extended in the transverse direction of a grid (47) are arranged at the same interval as a grid (47), and two or more tube support plates (49) extended to the lengthwise direction of a grid (47) are arranged at the same interval as a grid (47) between the grid (47) and the lower glass board (42).

[0005]
Although the issue of some, such as reduction of driver voltage and equalization of electron emission, which should be solved occurs by realization of carbon nanotube FED, the FED panel which formed the carbon nanotube negative pole by screen-stencil is made as an experiment.
[0006]
[Problem(s) to be Solved by the Invention]

In the above-mentioned conventional FED panel which formed the carbon nanotube negative pole by screen-stencil. When the inorganic matter of 1 one carbon nanotube came out scatteringly and imposed an electric field for a certain reason, the electric field concerning 1 one carbon nanotube became uneven, field emission became uneven as the result, and there was a problem that a display screen was coarse and luminosity was insufficient.

[0007]

Although it replaces with screen printing and the thin film of catalyst metal is patterned after the substrate of silicon or glass, a carbon nanotube is grown up in the shape of a brush with a CVD method by making it into a seed crystal and the trial which is going to apply this to an electron emission element is also performed, From growing up bending horizontally the brush-like carbon nanotube grown-up with the CVD method twining each other. Even if the insulation was electrically carried out by patterning at the root with much trouble, brushes contacted, as a result, the pitch of patterning could not be narrowed, but there was a problem that a display screen became coarse.

[0008]

When it is advantageous in cost and is used as an electrode of a field emission type flat-panel display toward mass production, the purpose of this invention, It is in providing an electrode material for electron emission elements using a carbon nanotube which can reduce driver voltage and can make a display screen fine, and a manufacturing method for the same.

[0009]

[Means for Solving the Problem]

In order to solve an aforementioned problem, this invention persons found out obtaining an electrode material for electron emission elements using a carbon nanotube by transferring a brush-like carbon nanotube grown up on a silicon substrate on a film by which a conductive layer portion was patternized.

[0010]

That is, an electrode material for electron emission elements by this invention is formed by transferring a carbon nanotube grown-up as a core in a catalyst particle on a substrate on a conductive film in which a conductive layer portion was patternized.

[0011]

A manufacturing method of an electrode material for electron emission elements by this invention transfers a carbon nanotube into which a catalyst particle on a substrate

was grown up as a core on a conductive film in which a conductive layer portion was patternized.

[0012]

Suppose that not only a film of a narrow sense specified as a "film" based on thickness but a thick thing usually called a sheet is included in this specification.

[0013]

In the above-mentioned electrode material and a manufacturing method for the same, a conductive layer may be formed by vapor-depositing a thin film of metal, such as silver, on a film made of resin etc., for example, and may form a pencil of a carbon nanotube by pasting up with a prescribed interval on a film made of resin. Having the advantage that production of a patternized conductive film is easy for the former, the latter has the advantage that extension of a patternized conductive film is easy and an interval of the carbon nanotubes transferred by adjusting an extension rate is easy.

[0014]

In the above-mentioned electrode material, as for the length of a carbon nanotube, 1-150 micrometers is preferred, and, as for an interval of carbon nanotubes, 10-1000 nm is preferred.

[0015]

It is preferred to transfer a carbon nanotube to a parenchyma top perpendicular direction to a film surface in a manufacturing method of the above-mentioned electrode material to a conductive film, It is preferred to make temperature of a conductive film in the case of transfer below into melting temperature above the softening temperature, and it is preferred to cool a conductive film below to the softening temperature after transfer further again.

[0016]

A manufacturing method of an electrode material for electron emission elements using a carbon nanotube by this invention can also be enforced continuously.

[0017]

A carbon nanotube is a substance of the shape of a very detailed pipe (tube) of made bore-diameter nano (1 nano is 1/1 billion) meter size where a carbon atom combined with mesh shape.

[0018]

A brush-like carbon nanotube is producible by a publicly known method. For example, on a coat heated and formed on one side at least after applying a solution of a silicon

substrate containing a complex of metal, such as nickel, cobalt, and iron, with a spray or a brush, Or a carbon nanotube 12-38 nm in diameter is napped vertically on a substrate by multilayer structure by using acetylene (C_2H_2) gas and giving general chemical vapor deposition (CVD method) on a coat struck and formed with a cluster gun.

[0019]

[Embodiment of the Invention]

Below, an embodiment of the invention is described.

[0020]

First, a catalyst particle is formed on a substrate and a carbon nanotube is grown up from material gas by a high temperature atmosphere by using a catalyst particle as a core. That [a substrate's] which supports a catalyst particle and in which a catalyst particle should not just get wet easily may be preferred, and it may be a silicon substrate. Catalyst particles may be metal particles, such as nickel, cobalt, and iron. The solution of compounds, such as these metal or a complex of those, is applied to a substrate with a spray or the brush, or with a cluster gun, it strikes against a substrate and it is dried, if required, it will heat, and a coat is formed. Since particle-ization by heating will become difficult if too thick, the thickness of a coat is 1-100 nm preferably. Subsequently, if this coat is heated at 650-800 ** preferably [it is desirable and] under decompression or in a non-oxidizing atmosphere, a catalyst particle about 1-50 nm in diameter will be formed. As material gas of a carbon nanotube, aliphatic hydrocarbon, such as acetylene, methane, and ethylene, can be used and acetylene gas is especially preferred. In the case of acetylene, a carbon nanotube with a thickness of 12-38 nm uses a catalyst particle as a core by multilayer structure, and it is formed in the shape of a brush on a substrate. The forming temperature of a carbon nanotube is 650-800 ** preferably.

[0021]

In this way, the brush-like carbon nanotube grown up is transferred to a conductive film. In the case of transfer, it becomes easy by making temperature of a conductive film below into melting temperature above the softening temperature of a conductive film to make the orientation of the carbon nanotube carry out perpendicularly to a conductive film. After transfer can fix a carbon nanotube to a conductive film by cooling the temperature of a conductive film below to softening temperature.

[0022]

The conductor of prescribed width should be provided in the

conductive film with the prescribed interval on the insulating resin sheet, for example. As an insulating resin sheet, the polyethylene film which has an ethylene vinyl alcohol layer at the rear face is illustrated, and metal, metallic carbon nanotubes, etc., such as silver, are illustrated as a conductor. Silver is formed by vacuum evaporation on an insulation sheet, for example, and a carbon nanotube is formed by adhesion on an insulation sheet.

[0023]

The above-mentioned process (namely, spreading of the catalyst to a substrate, formation of a catalyst particle, growth of the brush-like carbon nanotube by chemical vapor deposition, transfer to the conductive film of a carbon nanotube, subsequent film cooling) can be performed as a series of continuous processes. One embodiment at the time of carrying out as a continuous process is shown with reference to drawing 1.

[0024]

(The first process)

In the catalyst adhesion zone of the upper part upstream part of composition) in drawing 1, by a low resistance N-type semiconductor silicon substrate with an endless belt (3) (thickness of 0.5 mm rotated by feed-rate 12 m/h by driving drum (1) and follower drum (2), After applying the solution of Fe complex to the upper surface of an endless belt (3) by a spray (4), a catalyst particle (12) is made to form on an endless belt (3), by heating at 220 **, so that it may be scattered at intervals of 100 nm.

[0025]

(The second process)

Subsequently, the catalyst particle (12) on an endless belt (3) is sent to the chemical-vacuum-deposition zone of the catalyst adhesion zone lower stream. A chemical-vacuum-deposition zone consists of a heating furnace (5) which has a length of about 2 m in the move direction in the direction of a belt, and a warmer (7) arranged under the endless belt (3) in the inside. In a chemical-vacuum-deposition zone, acetylene gas is flowed into a heating furnace (5) by flow 30 ml/min from the crowning of a heating furnace (5) as material gas of a carbon nanotube, and the catalyst particle (12) on an endless belt (3) is heated in temperature of about 720 ** with the warmer (7) which circulates through a heat carrier from the bottom. Time for each catalyst particle to pass through a heating furnace (5) is made into about 15 minutes. A catalyst particle (12) takes for moving the inside of a heating furnace (5), a brush-like carbon nanotube (11)

generates on it by using a catalyst particle (12) as a core, and it grows up upward. The grown-up carbon nanotube is multilayer structure with a thickness of about 12 nm, and length is set to about 50 micrometers.

[0026]

(The third process)

The carbon nanotube (11) of each catalyst particle (12) on an endless belt (3) by movement of a belt Subsequently, the position of a chemical-vacuum-deposition zone to a follower drum (2), That is, it reaches to a transfer zone, and when following on turning around the outside of a follower drum (2) and falling horizontally gradually, a carbon nanotube (11) is pushed against a conductive film conductive film (8) from the tip. The conductive layer portion was patternized and a conductive film (8) consists of an insulating resin sheet (14) and a conductor (15) of the specified shape established on the sheet (14). As a conductive film (8) is more preferably shown in drawing 2, a resin sheet is made into the two-layer structure of a polyethylene layer (14a) and the ethylene vinyl alcohol layer (14b) provided in the rear face, and let a conductor (15) be a silver film of prescribed width. And the electric conduction pattern in which many band-like conductors (15) were arranged on the conductive film (8) in parallel is formed by providing the silver film of prescribed width with a prescribed interval on a polyethylene layer (14a). This conductive film (8) is sent downward from a film supply device (9), and is heated with a warmer (10) at more than the softening temperature of a resin sheet (14), and below melting temperature (for example, 100-300 **). In this way, by pushing a carbon nanotube (11) against a conductive film (8), a carbon nanotube (11) is vertically transferred by the conductive film (8) from a catalyst particle (12) on parenchyma to a film surface.

[0027]

(The fourth process)

The conductive film (8) in which the brush-like carbon nanotube was planted by transfer is cooled below to the softening temperature (for example, ordinary temperature) with the condensator (13) in which it was provided under the warmer (10). And an endless belt (silicon substrate) (3) is removed from a carbon nanotube (11) after cooling. In this way, the obtained carbon nanotube electrode is rolled round by the coiling drum (6).

[0028]

The structure of said carbon nanotube may be a monolayer, i.

e., a single tube, and may be a multilayer, i.e., two or more concentric different diameter tubes. The diameter of a carbon nanotube is 1-100 nm preferably.

[0029]

In order to produce a brush-like carbon nanotube with a CVD method, An iron metal catalyst is required as a seed crystal, and in order that a carbon nanotube may grow on a catalyst, the adhesive strength between a substrate and a carbon nanotube is weak, Since it is immersed in electrolysis solutions, such as acid and alkali, when using it for a capacitor etc., a carbon nanotube may separate from a substrate while in use. A brush-like carbon nanotube is lacking in linearity, in order to grow up twining each other. Although methods, such as carrying out vertical **** of the carbon nanotube by direct-current glow discharge, are proposed by JP,10-203810,A, this is not fit for industrial production. A brush-like carbon nanotube has unevenness in the apical surface of a brush, and is not level to it.

[0030]

The temperature of the conductive film at the time of planting in a conductive film the carbon nanotube grown up on the substrate in a transfer process, in order to solve many above problems 70-140 **, It is good for 50-0 ** of temperature at the time of removing a substrate from the carbon nanotube which was 80-120 ** preferably and was planted in the conductive film to be 35-0 ** preferably. As for a conductive film, it is preferred that it is a multilayer film which contains at least the layer which supports a polyethylene layer and a same layer. As for the layer which supports a polyethylene layer, consisting of a heat-resistant film is preferred. As for a heat-resistant film, it is preferred that it is a polyethylene terephthalate film.

[0031]

The carbon nanotube produced by this invention became clear [having the characteristic which was dramatically excellent as an electric field electron emitter]. Namely, although the carbon nanotube as an electron emission raw material has the outstanding features, such as that restrictions of a vacuum are loose, that high current density is obtained, and a stout thing, compared with micro emitters, such as silicon and molybdenum, in recent years, When the brush-like carbon nanotube which grew up to be a silicon substrate was used, in order that the carbon nanotube might twine each other also in a vertical direction to the growth direction of a carbon nanotube, there was a problem that the voltage at the time of taking out an electron that the electrical and electric equipment leads easily was high. To

it, in order for carbon nanotubes not to twine, also when an electric field low as the result is imposed, it becomes easy to emit electrons from the tip of a carbon nanotube according to this invention that the electrical and electric equipment cannot pass easily (conductivity is bad) in a direction vertical to a growth direction.

[0032]

Below, this invention is concretely explained based on an example.

[0033]

Example 1

(The first process)

After thickness applied the solution of $Fe(CO)_5$ by a spray at 0.5 mm on the rectangular silicon substrate whose one side is 100 mm, the iron coat was made to generate by heating at 220 **.

[0034]

(The second process)

The substrate with an iron covering film was put into the chemical vapor deposition system. As material gas of a carbon nanotube, the mixed gas of acetylene of flow 3 ml/min and gaseous helium of flow 200 ml/min was passed in the chemical vapor deposition system for the temperature of 720 **, and time 15 minutes. The brush-like carbon nanotube generated by having used as the core the catalyst particle obtained by particle-izing an iron covering film with this heating, and it grew up gradually. The grown-up carbon nanotube was multilayer structure with a thickness of 12 nm, and length was 50 micrometers.

[0035]

(The third process)

Thickness produced the conductive film in which one side patternized the surface at 20 micrometers by vapor-depositing a silver film with a thickness of 10 nm patternized at 100 micrometers in width to the rectangular polyethylene film (what has an ethylene vinyl alcohol layer at the rear face) which is 100 mm.

[0036]

(The fourth process)

The carbon nanotube was vertically transferred on parenchyma to the film surface by pushing from a tip the brush-like carbon nanotube produced at the second process against the patternized conductive film which was obtained at the third process heated at 95 **.

[0037]

(The fifth process)

The electrode material for electron emission patternized by removing a silicon substrate was obtained after cooling the conductive film in which the brush-like carbon nanotube was planted by transfer at 30 **.

[0038]

thus, when the produced electrode material for electron emission was used for the FED panel structure shown in drawing 5, the display screen was markedly alike as compared with the conventional thing, and became fine. This is considered because electric field concentrates came to happen more strongly by the carbon nanotube's having carried out orientation straightly, and having torn the tip and moreover, having had a sharp edge by having removed the carbon nanotube from the substrate.

[0039]

Comparative example

(The first process)

Thickness produced what patternized the iron film by 100-micrometer width at photo lithography on the rectangular silicon substrate whose one side is 100 mm at 0.5 mm. .

[0040]

(The second process)

The substrate with the patternized iron covering film which was produced at the first process was put into the chemical vapor deposition system. As material gas of a carbon nanotube, the mixed gas of acetylene of flow 3 ml/min and gaseous helium of flow 200 ml/min was passed in the chemical vapor deposition system for the temperature of 720 **, and time 15 minutes. The brush-like carbon nanotube generated by having used as the core the catalyst particle obtained by particle-izing an iron covering film with this heating, and it grew up gradually. The grown-up carbon nanotube was multilayer structure with a thickness of 12 nm, and length was 50 micrometers.

[0041]

Thus, image quality was bad when the produced electrode material for electron emission was used for the FED panel structure shown in drawing 5. As this shows drawing 3, It thinks for the carbon nanotubes (21) grown-up from that the carbon nanotubes (21) formed on the glass substrate (20) twine each other, and high current density is not obtained at the tip of a carbon nanotube (21) and the adjoining iron catalyst particles contacting.

[0042]

Example 2

(The first process)

After thickness applied the solution of $Fe(CO)_5$ by a spray at 0.5 mm on the rectangular silicon substrate whose one side is 100 mm, the iron coat was made to generate by heating at 220 **.

[0043]

(The second process)

The substrate with an iron covering film was put into the chemical vapor deposition system. As material gas of a carbon nanotube, the mixed gas of acetylene of flow 3 ml/min and gaseous helium of flow 200 ml/min was passed in the chemical vapor deposition system for the temperature of 720 **, and time 15 minutes. The brush-like carbon nanotube generated by having used as the core the catalyst particle obtained by particle-izing an iron covering film with this heating, and it grew up gradually. The grown-up carbon nanotube was multilayer structure with a thickness of 12 nm, and length was 50 micrometers.

[0044]

(The third process)

the guttering (18a) of the polyethylene film (100 mm in width, 1000 mm in length, and 0.1 mm in thickness) (18) processed into conduit-like [100 micrometers-pitch], as a portion is made to deposit the bunch of a carbon nanotube (17) and it is shown in drawing 4, The conductive film (8) which patternized the surface was produced by turning the bunch of a carbon nanotube (17) to the resin sheet (16) side, and pasting this polyethylene film (18) together via a glue line (19).

[0045]

(The fourth process)

The carbon nanotube was vertically transferred on parenchyma to the film surface by pushing from a tip the brush-like carbon nanotube produced at the second process against the patternized conductive film which was obtained at the third process heated at 95 **.

[0046]

(The fifth process)

The electrode material for electron emission patternized by removing a silicon substrate was obtained after cooling the conductive film in which the brush-like carbon nanotube was planted by transfer at 30 **.

[0047]

thus, when the produced electrode material for electron emission was used for the FED panel structure shown in drawing 5, the display screen was markedly alike as compared with the conventional thing, and became fine.

This is considered because electric field concentrates came to happen more strongly by the carbon nanotube's having carried out orientation straightly, and having torn the tip and moreover, having had a sharp edge by having removed the carbon nanotube from the substrate. Since it has ductility, the electrode of this structure can respond also to curved-surface structure arbitrarily.

[0048]

[Effect of the Invention]

Since the detailed control of the conducting sleeve being carried out and use with high current density are possible according to this invention, it is applicable not only to a flat-panel display but an ultrahigh frequency device and the electron beam exposure which used the minute field emitter array.

[Brief Description of the Drawings]

[Drawing 1]It is a schematic diagram showing the continuous manufacturing method of a carbon nanotube electrode.

[Drawing 2]It is a sectional view showing the electrode material of Example 1 typically.

[Drawing 3]It is a sectional view showing the electrode material of a comparative example typically.

[Drawing 4]It is a sectional view showing the electrode material of Example 2 typically.

[Drawing 5]It is a perspective view showing the structure of the FED panel typically.

[Description of Notations]

(8) : conductive film
(9) : film supply device
(11): Carbon nanotube
(12): Catalyst particle
(14): Resin sheet
(15): Conductor
(16): Resin sheet
(17): The bunch of a carbon nanotube

[Translation done.]